DETERMINATION OF NO AND NO_2 IN CIGARETTE SMOKE FROM KINETIC DATA

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A method of estimating the amounts of nitrogen oxides in cigarette smoke at the time the smoke exits from the cigarette is presented. It is based on evidence that the oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2) in diluted cigarette smoke is a psuedo second-order reaction because a large excess of oxygen is present. Data are presented to support this observation. On the basis of this method, the amount of NO_2 in smoke from a commercial cigarette was estimated to be 15 μg; the amount of NO was 250 μg. Filters of paper cellulose acetate, or charcoal did not reduce the amount of NO or NO_2 in cigarette smoke. Smoke from cigarettes high in nitrates had higher amounts of nitrogen oxides than cigarettes low in nitrates. The amount of nitrogen oxides found by analysis of individual puffs was twice that found by analysis of the combined puffs from a cigarette of the same type.

INTRODUCTION

Various techniques for the analysis of nitrogen oxides in cigarette smoke have been reported (1, 3, 6, 7, 9, 11, 13, 14). Most authors (1, 3, 6, 7, 13) agree on the amount of total oxides of nitrogen occurring in cigarette smoke, but they disagree on the individual amounts of nitric oxide (NO) and nitrogen dioxide (NO_2). Norman and Keith (7) reported that the predominant species was NO and that NO_2 was present only in trace quantities. Barkemeyer and Seehofer (1) recently reported that NO was the major nitrogen oxide. Other authors (3, 6, 13) have reported that up to 50% of the total oxides in nitrogen in cigarette smoke is NO_2.

Since there is considerable interest in the ratio of NO to NO_2 in cigarette smoke, a new method for the analysis of these components to supplement the information already in the literature was considered desirable. The method developed in this study is based on the rate at which NO is oxidized to NO_2. The rate of conversion of NO to NO_2 in dilute cigarette smoke is measured colorimetrically. The data are treated kinetically, and the ratio of NO to NO_2 is calculated from the rate equations.

MATERIALS AND METHODS

Reagents. The modified Griess reagent was an aqueous solution of 14% acetic acid, 5% sulfanilic acid, and 0.02% N-(1-naphthyl)ethylenediamine dihydrochloride prepared and stored as described by Saltzman (10).

Nitric oxide and nitrogen dioxide were obtained from Air Products Company.

Calibration solutions were aqueous solutions of sodium nitrite.

Cigarettes. The cigarettes (85-mm) used in the experiments were conditioned to 12% ((± 1%) moisture content and selected to be within 20 mg of their average weight. The cigarettes represented burley, bright, and blended tobaccos. One group of the blended cigarettes contained 8% sodium nitrate.

Filters. Paper, cellulose acetate, and activated charcoal filters were tested on the blended cigarettes. The paper and acetate filters were 20 mm long, and the charcoal filter consisted of 100 mg of activated charcoal held in 5-mm space between two 7.5-mm acetate plugs.

Apparatus. The reaction vessel was a 280-ml gas sampling bottle modified with a side arm and serum cap.

The spectrophotometer was a Beckman Model B equipped with 10-mm cuvettes.

EXPERIMENTAL

Absorption Rate of NO_2 in Griess Reagent. Approximately 60 μg of NO_2 was injected into the reaction vessel which contained 50 ml of Griess reagent. The vessel was shaken vigorously and samples were then withdrawn periodically, diluted with 4 parts of water, and allowed to stand 15 min.

Absorbance of the solution, which is a function of the pink color produced by reaction of NO_2 with Griess reagent, was determined on the Beckman Model B spectrophotometer at a wavelength of 550 mμ. The amount of NO_2 in each sample was read from a calibration curve.

Oxidation Rate of Known Samples of NO. The oxidation rate of known samples of NO was measured at three different concentrations of oxygen—namely, 10, 16, and 20%. These levels were selected to cover the range expected in dilute cigarette smoke.

Approximately 60 μg of NO was injected into the reaction vessel, which contained 50 ml of Griess reagent and nitrogen at 360 mm pressure. Measured amounts of oxygen and additional nitrogen were added to adjust the gas mixture in the reaction vessel to atmospheric pressure. The vessel was shaken on an automatic shaker, and samples of reagent were removed at intervals of 15, 30, 45, 60, 180, and 360 sec for determination of NO_2. The final sample was taken after 90 min; after this time, conversion of NO to NO_2 was practically quantitative.

Oxidation Rate of NO in Dilute Cigarette Smoke. The reaction vessel was charged with 50 ml of Griess reagent, and the bottle was evacuated. One outlet of the bottle was connected to an automatic syringe-type smoking machine which drew a single 35-ml puff from a cigarette and injected it into the bottle. The bottle was immediately disconnected from the smoking machine, and air was admitted to provide oxygen for oxidation of the NO in the smoke. The bottle was shaken, and samples of reagent were then withdrawn and analyzed for NO_2.

Calculations. The reaction of NO and O_2 is third order (5) and is expressed by the equation

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

The rate equation for this reaction is

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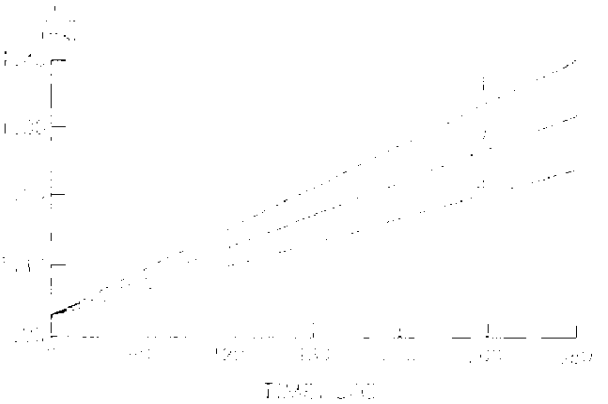

Figure 1—Effect of oxygen concentration on conversion rate of NO to NO_2. Curve 1—20% O_2; slope, 10.79 × 10^{-4}; NO_2, 2.3 μg. Curve 2—16% O_2; slope, 8.38 × 10^{-4}; NO_2, 2.7 μg. Curve 3—10% O_2; slope, 6.95 × 10^{-4}; NO_2, 1.9 μg.

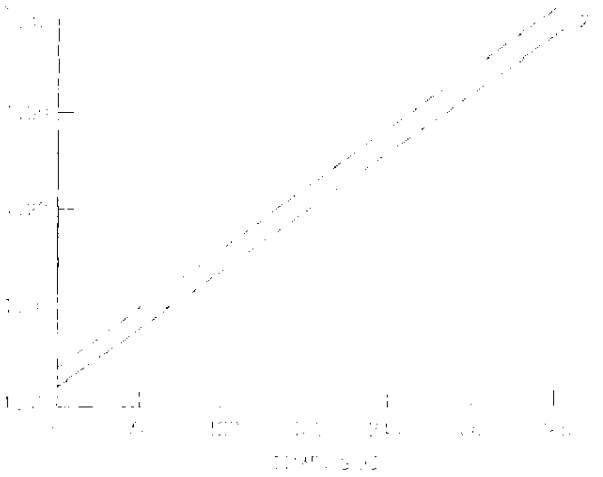

Figure 2—Oxidation rates of NO in air and NO in dilute cigarette smoke. Curve 1—NO in air; slope, 10.79 × 10^{-4}; NO, 53.9 μg, NO_2, 2.3 μg. Curve 2—NO in dilute cigarette smoke; slope, 10.25 × 10^{-4}; NO, 73.0 μg, NO_2, 1.3 μg.

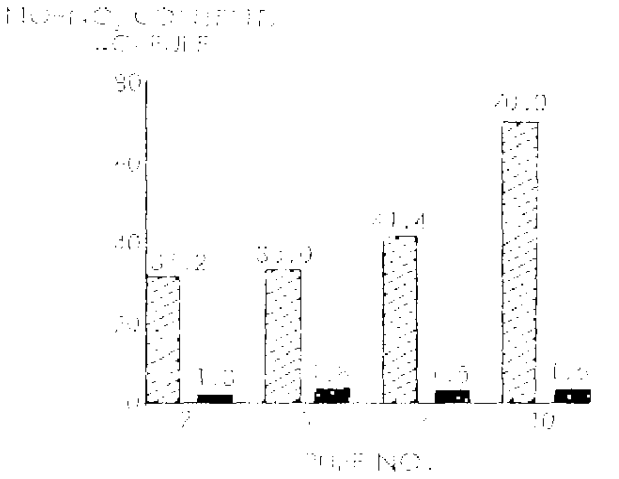

Figure 3—NO-NO_2 content of smoke from a commercial cigarette. □=NO. ■=NO_2.

$$\frac{d\left[C_{NO_2}\right]}{dt} = k[C_{O_2}]\,[C_{NO}]^2 \qquad (2)$$

If x = mole fraction of NO_2 and $C_t = C_{NO} + C_{NO_2}$, equation 2 becomes

$$\frac{dx}{(1-x)^2} = k[Co_1]\;[C_t]dt \qquad (3)$$

Since $[CC_0]$ is virtually constant, the reaction is pseudo second order, and integration of equation 3 gives

$$\frac{1}{(1-x)} = k[Co_2]\;[C_t]t + \frac{C_t}{C_{NO}^0} \qquad (4)$$

The experimental data are shown in **Figure 1**, where values for the left-hand term of the integrated rate expression are plotted against time. The curve was fitted to the data points by a regression analysis. From the data, the slope of the curve and integration constant (intercept) were evaluated. These values were substituted in equation 4 to determine the mole fraction of NO_2 at time zero (x_0). From the stoichiometry of the process, it follows that x_0 multiplied by the total amount of nitrogen oxides, calculated as NO_2, is equal to the amount of NO_2 in the sample at time zero.

The numerical values found for the slopes of the curves are not absolute rate constants but are the values for the expression k $[C_{O_2}]$ $[C_t]$.

The rate constant *k* was calculated from our experimental data to be 1.6 x 10^{10} cc^2-$moles^{-2}$-sec^{-1} for a known sample of NO and 1.1 × 10^{10} cc^2-$moles^{-2}$-sec^{-1} for the NO in cigarette smoke. Frost and Pearson (5) reported 8 × 10^9 cc^2-$moles^{-2}$-sec^{-1}. Benson (2) reported a pre-exponential factor log A of 3. 02 $liters^2$/moles-sec and an activation energy of —1.1 kcal/mole. From these data, a rate constant of 1.65 × 10^8 cc^2-$moles^{-2}$-sec^{-1} was calculated.

RESULTS AND DISCUSSION

Absorption of NO_2 by Griess Reagent. The rate of absorption of NO_2 in Griess reagent in the reaction vessel was very rapid compared to the rate of oxidation of NO. Over 90% of the NO_2 was absorbed in 15 sec, and absorption was quantitative in 30 sec; therefore, Griess reagent was used to study the rate of oxidation of NO.

The NO_2-from a sodium nitrate solution used for calibration gave a color intensity with Griess reagent equal to that produced by a molar equivalent of NO_2. This stoichiometric relation was also obtained by Stratmann and Buck (12) but not by Saltzman (10), who reported a conversion efficiency of 72%.

Effect of Oxygen Concentration on Reaction Rate. The concentration of oxygen in the reaction vessel covered the range expected in cigarette smoke. It influenced the NO oxidation rate, as illustrated by **Figure 1.** This behavior is consistent with the established third-order reaction mechanism (5); however, the rate of disappearance of the NO with time is a pseudo second-order reaction in the experiments because the change in oxygen concentration during the reaction is negligible. In each of the three experiments, the amounts of NO_2 found in the NO ranged from 1.9 to 2.7 μg, probably because this compound was present as an inpurity in the NO.

The oxidation rate of NO in dilute cigarette smoke is very close to that of NO in air. Typical rate curves, this compound was present as an impurity in the NO.

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shown in Figure 2, represent a sample of NO from a lecture cylinder and a sample of NO in cigarette smoke. Both samples were diluted with sufficient air to obtain an oxygen content of 20%.

Since the slopes are about equal, reaction of the formed NO_2 with other smoke components is not sufficient to introduce a significant error in the NO_2 determination; therefore, we assumed that the rate of formation of NO_2 is equal to the rate of disappearance of NO.

Analysis of Smoke From Commercial Cigarettes. The second, fifth, seventh, and tenth puffs of an 85-mm commercial cigarette were analyzed for NO and NO_2. The results are shown in **Figure 3.** The amount of NO increased with each succeeding puff (31.2 μg for first puff to 70 μg for last puff), but the NO_2 did not increase significantly. The standard deviations were 9.04 for NO and 0.14 for NO_2.

When the total amount of smoke vapor from the cigarette was trapped and analyzed, 275 μg of nitrogen oxides was obtained. This amount is about half that obtained when separate puffs were analyzed and the values totaled. This difference indicates that some reaction is taking place between the NO and other smoke components during the collection of the smoke vapors.

Norman and Vinson (8) reported that aldehydes, isoprene, and hydrogen sulfide react with the oxides of nitrogen. In our study, we found that methyl mercaptan also reacts with nitrogen oxides.

Effect of Nitrates in Tobacco on the NO and NO_2 Contents of Cigarette Smoke. The oxides of nitrogen in cigarette smoke are directly related to the nitrate content of the tobacco (4). This relation is shown in **Figure 4.**

Smoke from the low-nitrate bright leaf tobacco (0.10% nitrate) contained an average of 4.0 μg NO and 0.3 μg NO_2 per puff; the values for cigarettes containing added nitrate (5.8% nitrate) were greater than 200 μg NO and 10μg NO_2 per puff.

Effect of Filters on the NO and NO_2 Contents of Cigarette Smoke. The amounts of NO and NO_2 delivered by cigarettes equipped with paper, cellulose acetate, and charcoal filters are shown in **Figure 5.** None of the filters was effective in removing either NO or NO_2 from cigarette smoke.

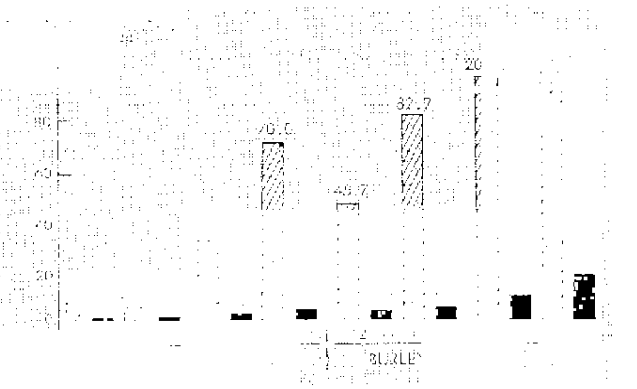

Figure 4—Effect of nitrate in tobacco on the NO-NO_2 content of cigarette smoke. □=NO. ■=NO_2.

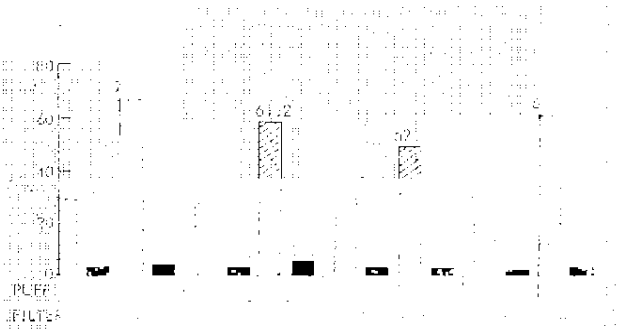

Figure 5—Effect of filters on NO-NO_2 content of cigarette smoke. □=NO. ■=NO_2.

SUMMARY

A new technique, based on kinetic data, is presented for the determination of NO and NO_2 in cigarette smoke. The oxidation rate of known samples of NO diluted with specific concentrations of oxygen and nitrogen is compared to the oxdation rate of NO in cigarette smoke containing similar amounts of added oxygen.

The amount of NO_2 in cigarette smoke is relatively low compared to the amount of NO present. Both depend on the amount of nitrate in the tobacco. The average amount of NO and NO_2 per 35-ml puff of a commercial cigarette was 44μg and 1.5 μg, respectively.

The amount of nitrogen oxides per cigarette obtained by analyzing the individual puffs was about twice the amount found by analysis of the combined puffs from a cigarette of the same type.

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